

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

1 1 1 1 1 1 1 1 1 1 1 1 1



CHEMICAL
RESEARCH,
DEVELOPMENT &
ENGINEERING
CENTER

AD-A172

FILE COPY

CRDEC-TR-86052

POLYSTYRENE LATEX AEROSOL: NOT NECESSARILY MONODISPERSED

by Gregg W. Adams
Patrice E. Simmons
RESEARCH DIRECTORATE

July 1986



U.S. ARMY ARMAMENT MUNITIONS CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland 21010-5423

This document has been approved for public release and sale; he distribution is unlimited.

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

Distribution Statement

Approved for public release; distribution unlimited.

SECURITY CLASSIFICATION OF THIS PAGE		P 10-1	7111	701		
	REPORT DOCUM	MENTATION	PAGE			
1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS				
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT				
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		Approved for public release; distribution unlimited.				
4. PERFORMING ORGANIZATION REPORT NUMBER(5)		5. MONITORING ORGANIZATION REPORT NUMBER(S)				
CRDEC-TR-86052						
6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION				
CRDEC	SMCCR-RSC-A					
6c. ADDRESS (City, State, and ZIP Code)		7b. ADDRESS (City, State, and ZIP Code)				
Aberdeen Proving Ground, MD 21010-5423						
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER				
CRDEC	SMCCR-RSC-A					
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS				
Aberdeen Proving Ground, M	21010-5423	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT	
			1L162706	A553	<u>l</u>	
11. TITLE (Include Security Classification)	-					
Polystyrene Latex Aerosol:	Not Necessa	rily Monod:	ispersed			
12. PERSONAL AUTHOR(S) Adams, Gregg W., and Simmon	ns, Patrice E.	,				
13a. TYPE OF REPORT 13b. TIME COVERED 14. DATE OF REPORT (Year, Month, Day) 15. PAGE COUNT Technical FROM 84 04 TO 84 07 1986 July 15						
16. SUPPLEMENTARY NOTATION						
17. COSATI CODES	18. SUBJECT TERMS (C Polystyrene	Continue on reverse if necessary and identify by block number)				
FIELD GROUP SUB-GROUP 15 02		latex Electrostatic classifier d aerosol Condensation nucleus counter				
	Differential		nalyzer			
19. ABSTRACT (Continue on reverse if necessary						
The use of polystyrene lat	ex (PSL) sphe	res as a mo	onodispers	ed aerosol	from	
atomization of the suspens						
performance characteristics of an electrostatic aerosol classifier. Problems encountered with the monodispersity of the aerosol due to particle aggregates,						
suspension residue, drying	of the atomi:	zed spheres	, and part	ticulate i	mpurities	
in the distilled water used for dilution were examined. The causes of these						
problems are presented and their previous history in the scientific literature						
shown.						
\ <u>'</u>						
· ·						
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT 21. ABSTRACT SECURITY CLASSIFICATION						
■ UNCLASSIFIED/UNLIMITED □ SAME AS F	UNCLASSIFIED					
22a NAME OF RESPONSIBLE INDIVIDUAL TIMOTHY E. HAMPTON	226. TELEPHONE ((301) 6	include Area Code 71-2914) 22c. Office SY SMCCR-	MBOL -SPD-R		
والمتراب المتناق أأني والشار والمتراب المتناق المتناق المتناق المتراب المتراب والمتناق والمتناق المتناق المتناق	Redition may be used un All other editions are of		SECURITY	CLASSIFICATION C	OF THIS PAGE	

PREFACE

The work described in this report was authorized under Project 1L162706A553, CB Defense and General Investigations, Technical Area 3-D, Individual Protection. The experimental work was performed between April and July 1984.

The use of trade names or manufacturers' names in this report does not constitute endorsement of any commercial products. This report may not be cited for purposes of advertisement.

Reproduction of this report in whole or in part is prohibited except with permission of the Commander, U.S. Army Chemical Research, Development and Engineering Center, ATTN: SMCCR-SPD-R, Aberdeen Proving Ground, Maryland 21010-5423. However, the Defense Technical Information Center and the National Technical Information Service are authorized to reproduce the document for U.S. Government purposes.

This report has been approved for release to the public.

Acces	sion For		
NTIS	GRA&I	*	
DTIC TAB			
Unannounced 🔲			
Justi	fication_		
	ibution/	Codes	
Dist	Avail an Specia	•	
DIST	Specia	-	
A-1			



Blank

CONTENTS

		Page
1.	INTRODUCTION	7
2.	BACKGROUND	7
3.	MEASUREMENTS AND DISCUSSION	9
4.	CONCLUSIONS	14
	LITERATURE CITED	17
	LIST OF FIGURES	
Figure		
1	Initial Test Results with 0.085-PSL Solution	10
2	Initial Measurement of the 0.101-PSL Solution	12
3	Size Distribution of Particles Present in the Laboratory Distilled Water	12
4	Size Distribution of Particles in the Commercially Distilled Water	12
5	The 0.109-Micron PSL in Commercially Distilled Water	13
6	The 0.220-Micron PSL in Commercially Distilled Water	13
7	The 0.312-Micron PSL in Commercially Distilled Water	13
8	The 0.085-Micron PSL in Commercially Distilled Water	14

ACCOUNT OF THE PROPERTY OF THE

Blank

POLYSTYRENE LATEX AEROSOL: NOT NECESSARILY MONODISPERSED

1. INTRODUCTION

The use of Polystyrene Latex (PSL) as a highly monodispersed aerosol has become a common practice in aerosol technology. These pre-sized particles, in dilute suspensions, are atomized and then dried for use in the testing and calibration of optical, electrical, and inertial aerosol measuring equipment. Since the PSL spheres are sized by the manufacturer and their containers labeled with both the diameter and standard deviation, the aerosols produced are usually considered to be monodispersed. This is not always true, since a number of factors may cause the atomized aerosol to deviate from labeled size. PSL spheres are produced by a controlled emulsion polymerization process. The spheres are then sized by electron microscopy and sold in water suspensions of 10 percent solids. To prevent agglomeration of the spheres in the solution, an anionic surfactant is added. Seragen Diagnostics, formerly Dow Diagnostics, produces PSL particles and reports a high degree of accuracy in the measurement of their size.

This paper briefly examines the previous literature on PSL aerosol and describes a series of tests performed with a commercial electrostatic classifier. Problems encountered with the aerosol size and their resolution are presented. It is shown that care must be exercised to provide a monodispersed aerosol.

2. BACKGROUND

Previous authors have reported the existence of problems when using PSL aerosols. An excellent study of inherent problems with atomizing PSL suspensions is presented by Fuchs, ¹ Hinds, ² and Raabe. ³ Despite these and other published warnings, it is frequently inferred that the package labeling of the suspensions, which lists mean diameter and standard deviation, applies to the atomized aerosol as well as to the PSL aerosols. These label measurements are actual measurements of the PSL spheres, not of an aerosol.

The sizing technique employed by the manufacturer, electron microscopy, does not always agree with similar measurements performed by other investigators. Measurements made with low-intensity electron beams by Porstendörfer and Heyder showed sizes as much as 21 percent different than those of the manufacturer. The difference could result from swelling of PSL in the electron microscope beam; this is indicated since the measurements referred to were generally less than those reported by the manufacturer (beam intensity not given). Also observed was the evaporation of

PSL particles in the higher energy electron beams. This could lead to condensation on the other particles not directly in the beam, causing an apparent increase in their size. Accurate measurement of the size of PSL spheres requires careful examination with low-intensity electron beams, a tedious job and one that is usually neglected. The investigator, instead, relies on the accuracy of Seragen/Dow measurements.

The atomization process itself can produce particles of various sizes. If the dilution of the suspension is insufficient, a substantial number of droplets containing more than one sphere may be produced. When these multiplets are dried, the spheres agglomerate, producing aggregates of several spheres. For electron microscope measurements, this is not a problem since the aggregates are distinguishable. When light scattering, inertial, or electrical mobility measurement devices are used, these aggregates can completely alter the measurements, especially if the aerosol is assumed to be monodispersed. Hinds² gives the following formula for calculating the number of spheres per droplet:

$$X = F_v \left(\frac{d_\alpha}{d_p} \right)^3$$

where F_v is the volume fraction of spheres of diameter d_p and d_α is the diameter of the droplet. The probability of n spheres occurring in the droplet is given by:

$$P = X^n/n!e^{-X}$$
.

From these idealized equations, one can estimate the percentage of agglomerates of given size. The dilution of the suspension, $\mathbf{F_{v}}$, will determine the percentage of drops containing a given number of PSL spheres. While a greater dilution ratio will lead to fewer agglomerates, it will also result in a larger percentage of empties, droplets with no PSL spheres.

The empties themselves may result in particles of differing size. This is caused by the anionic surfactant present in the suspension. After these droplets are dried, the surfactant residue remains as an aerosol particle. If electron microscopy is used to size the particles, these empties present no problem, being clearly distinguishable from PSL spheres. Once again, optical or electrical mobility measurements may distort the results. While the residue particles are generally very small, they can be present in large concentrations. Many investigators have ignored the presence of these residue particles because of their small size, but for PSL spheres of less than 1.0 micron, the residue and PSL may be of similar size. In this case, neither optical nor electrical mobility measurements will be able to distinguish PSL spheres from the residue.

Another factor in determining the size of the particles after atomization is the drying of the droplets. If they are not completely dried, the remaining liquid increases the size of the PSL aerosol. The majority of investigators assume that the droplets are dried completely, leaving only the PSL spheres and residue particles. This assumption is clearly open to question; however, there is no easy way to verify the dryness of the spheres. Capture of particles and examination by electron microscopy may result in evaporation of the liquid, thus providing erroneous results that indicate dry spheres. Only great care in drying can assure that the PSL spheres are indeed dried.

3. MEASUREMENTS AND DISCUSSION

A TSI Model 3071 Electrostatic Classifier (EC) was tested with PSL aerosols. Several sizes of PSL spheres, 0.085, 0.312, and 0.497 micron, were obtained for testing. It was assumed that these three sizes would provide sufficient check on the operation of the EC. Since the TSI Model 3071 has a reputation for product quality, it was originally thought that this test would be straightforward and serve as a useful introduction to the EC. This did not prove to be the case.

The experimental apparatus used was a TSI Differential Mobility Particle Sizer (DMPS), which consists of the TSI Model 3071 Electrostatic Classifier, TSI Model 3020 Condensation Nucleus Counter, and the Apple IIe Computer. The microcomputer is used to control the operation of the DMPS, record the count from the Condensation Nucleus Counter, and reduce the data.

Polystyrene latex aerosols were atomized with a TSI Model 3046 Tri-Jet Aerosol Generator that was specifically designed for atomization of suspensions such as PSL. By having three atomizer systems with a common output, the Tri-Jet can be used to generate three different size ranges, or three different compositions of aerosols, individually or simultaneously.

Polydispersed aerosol from the generator enters the EC through an impactor. The impactor is used to minimize interference from multiply charged particles outside the mobility channel of the DMPS. A significant fraction of aerosol particles outside of the cut size of 0.808 micron are removed while particles within the measuring range of the DMPS follow the flow. Flow rates must be set carefully to ensure that turbulent flow is avoided. Proper operation of the EC requires that a laminar sheath of clean air be formed around the aerosol flow, which will then be laminar as well.

The monodispersed aerosol leaving the EC is directed into the Condensation Nucleus Counter (CNC) to measure the number concentration of aerosol particles. This is achieved by passing each particle through a saturated butyl alcohol vapor that condenses, causing droplets to grow to approximately 12 microns in diameter.

The theory and operation of the EC have been thoroughly treated by Knutson and Whitby 5 and Hoppel. 6 Of special interest to this work was the statement by Knutson and Whitby of a PSL dilution ratio of 2000:1, a factor of 20 times that which had been used initially in our work. This was the first indication that a problem might exist in the atomization of the aerosol. Having examined the previous experimental verification by these authors, it was felt that the equipment was performing properly, and that the results were due to the size of the aerosol.

For the next test, sizes of 0.109, 0.312, and 0.220 micron of PSL were obtained. Dilutions of one drop per 500 milliters to one drop per 1000 milliters of distilled water were used. Despite these steps, a wide range of particle sizes was observed. the smaller sizes were anticipated as being the result of surfactant residue, the larger particles were still present in numbers too large to be ignored, as shown in Figure 2. In order to determine the background aerosols present in the distilled water, data was taken with water only, no PSL, in the atomizer. Figure 3 shows the wide range of particle sizes found from the particulates present in the water. A second source of distilled water was obtained and used in the atomizer; the results are shown in The first source was a laboratory still, and the other water was commercially distilled. From these results it was decided to repeat the PSL experiments using the commercially distilled water, since the laboratory water was found to consistently contain a significantly greater amount of impurities.

Figures 5, 6, and 7 show the size distributions for the 0.109-, 0.220-, and 0.312-micron PSL aerosol, respectively. Before these measurements were made, the dessicant in the diffusion dryer was checked each time to ensure that it was not already moisture laden. It should be noted that the computer software does not necessarily match the measured diameters with the values given on the PSL samples. For the 0.312-micron PSL, the software actually skipped the PSL size, and the EC voltage had to be hand-tuned in order to find the PSL peak. The graphs show that the PSL size does not correspond to the peak size found by the EC for each sample. The graphs also show the continued existence of the residue aerosols and some larger particles, which may themselves be larger residue particles or aggregates formed from the presence of more than one PSL sphere in a drop.

As a final check, a sample of the 0.085-micron PSL was used again. The dilution ratio was one drop to 500 milliters; the diffusion dryer dessicant was fresh; and the distilled water was from the same source used above. As is shown in Figure 8, the PSL aerosol was well defined among the background of residue particles and aggregates. Since this sample was not placed in an ultrasonic mixer, the original assumption of PSL agglomeration on the shelf is false. The problems with the initial data sets were those enumerated above: dilution ratio, drying, residue aerosol, and the purity of the distilled water.

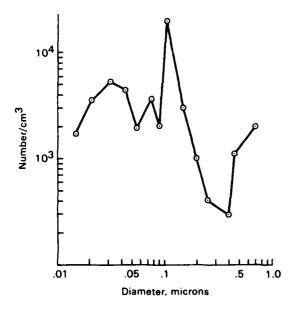


Figure 2. Initial Measurement Measurement of the 0.109-Micron PSL Solution

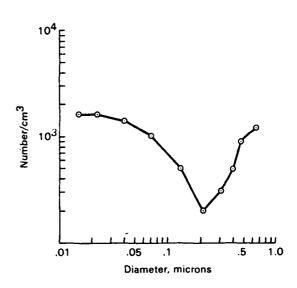


Figure 3. Size Distribution of Particles
Present in the
Laboratory Distribution

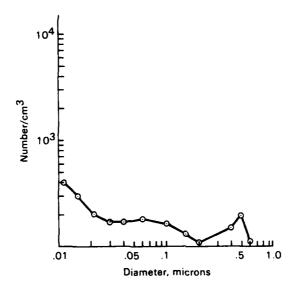


Figure 4. Size Distribution of Particles in the Commercially Distilled Water

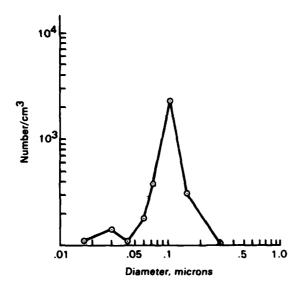


Figure 5. The 0.109-Micron PSL in Commercially Distilled Water

Figure 6. The 0.220-Micron PSL in Commercially Distilled Water

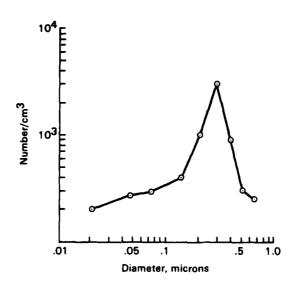


Figure 7. The 0.312-Micron PSL in Commercially Distilled Water

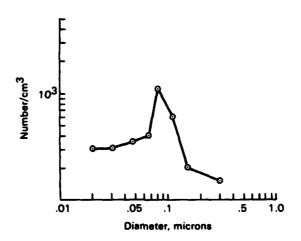


Figure 8. The 0.085-Micron PSL in Commercially Distilled Water

4. CONCLUSIONS

Several potential problems exist in the use of PSL as a monodispersed aerosol. If the measurement of size by the manufacturer is correct, the problems arise primarily from the atomization process. The existence of a considerable number of particles of sizes different than those of the actual PSL spheres means that the atomized aerosol is not truly monodispersed. This is an important factor if the PSL is being used to calibrate an optical particlesizing device. For any use, the spread of particle sizes must be recognized, and potential problems have to be assessed on a case-to-case basis.

LITERATURE CITED

- 1. Fuchs, N. A. J. Aerosol Sci. 4, 405 (1973).
- 2. Hinds, William C. Aerosol Technology. John Wiley & Sons. New York, NY. 1982.
- Raabe, Otto G. in <u>Fine Particles</u> edited by B. Y. H. Lui. Academic Press. New York, NY. 1976.
- 4. Porstendörfer, J., and Heyder, J. J. Aerosol Sci. 3, 141 (1972).
- 5. Knutson, E. O., and Whitby, K. T. J. Aerosol Sci. 3, 443 (1975).
- 6. Hoppel, W. A. J. Aerosol Sci. 9, 41 (1978).
